Nanoscale selective area epitaxy of C₆₀ crystals on GaAs by molecular beam epitaxy

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Abstract

Fabrications of nanoscale structures of C₆₀ crystals on GaAs substrates are successfully achieved by selective area molecular beam epitaxy. The grown structures are examined by scanning electron and atomic force microscopies. The {100} and {110} facets appear at the side boundaries of the C₆₀ crystals. The surface morphology of C₆₀ crystals grown on GaAs (111)B is much smoother than that grown on GaAs (001). Good crystalline properties of C₆₀ films grown on GaAs (111)B are also confirmed by X-ray diffraction ϕ (phi) scan measurement. During C₆₀ deposition, C₆₀ molecules landing on SiO₂ mask either evaporate or migrate to the open area enhancing the growth rate at the edges of the area. The mean diffusion length of C₆₀ molecules on SiO₂ mask at 200 °C is evaluated to be 200-300 nm. The C₆₀ crystals grown on GaAs (001) with narrow open area (100-200 nm) have a four-fold symmetry, indicating that the epitaxial orientation of these C₆₀ crystals is [001]. This result should be compared with the [111] orientation observed in planar or wide area growth.

1. Introduction

Extensive investigations have been done for the physical and chemical

properties of C_{60} , and have revealed their potentiality in superconductivity [1] and magnetism [2]. The C_{60} molecule is highly symmetric and crystallizes into a face-centered cubic structure on the crystalline substrates such as Si and GaAs [3-6]. Although the heterointerfaces between C_{60} films and these crystalline substrates have large lattice mismatch, the quality of grown C_{60} crystalline films is confirmed to be surprisingly high. Indeed, we have successfully grown high-quality crystalline [111]-oriented C_{60} films on GaAs (001) and GaAs (111)B substrates [7]. In the present work, we intended to fabricate nanoscale structures such as quantum wires and dots using C_{60} . Since the C_{60} films are very fragile and chemically unstable, conventional techniques such as etching and ion milling are not suitable for the fabrication processes. The selective area epitaxy makes it possible to achieve damage-free fabrication. Therefore, we have performed selective area epitaxial growth of C_{60} crystals on GaAs (001) and (111)B substrates with nanoscale open areas by using SiO_2 mask. The structures are formed by electron beam (EB) lithography. The grown structures of the C_{60} crystals and the surface morphology are evaluated by scanning electron microscope (SEM) and atomic force microscope (AFM). In order to investigate the crystalline quality of the C_{60} films, x-ray diffraction (XRD) measurements are performed.

2. Experimental procedure

Nanoscale structures of C_{60} crystals are fabricated on SiO_2 masked substrates by solid source molecular beam epitaxy with background pressure of 10^{-10} Torr. A 40-nm-thick SiO_2 film is deposited on GaAs (001) and (111)B substrates by a

conventional sputtering technique. Open area of the SiO₂ mask in various forms (e.g. hexagons, lines & spaces, and dots) is formed by EB lithography and wet chemical etching. The masked GaAs substrates are mounted on Mo holder alongside an unmasked (planar) GaAs (001) substrate. The unmasked substrates are used to observe reflection high-energy electron diffraction (RHEED) patterns. The native oxide layers of the GaAs surface are removed by a thermal flash at 580 °C in As₄ atmosphere. After 2 x 4 RHEED patterns of the unmasked GaAs (001) substrate are confirmed, C₆₀ layer growth is performed at substrate temperature of 200 °C. 99.5% C₆₀ powder is used as the C₆₀ source. The beam equivalent pressure of C₆₀ is fixed at 1.0 x 10⁻⁷ Torr with the deposition rate of 0.23 Å/s. The film thickness is fixed at 180 nm and 450 nm. The grown structures of the C₆₀ crystals are investigated by SEM and AFM. Both the 2θ/ω scan and φ (phi) scan measurements are performed with the Cu-Kα radiation (λ=1.54056 Å).

3. Results and discussions

The RHEED patterns of C₆₀ films grown on GaAs (001) and GaAs (111)B substrates exhibit well characterized 1 x 1 structure and indicate that the epitaxial orientation is [111] direction on both substrates [7]. From the observed streak intervals of the patterns, the lattice constant of cubic C₆₀ coincides well with that of bulk cubic C₆₀ crystals [7, 8].

Figure 1 shows the SEM images of the hexagonal C₆₀ crystals grown on GaAs substrates at 200 °C. The thickness measured on the unmasked substrate is 180 nm.

Figures 1(a) and (b) show the C₆₀ crystals grown on GaAs (001) and GaAs (111)B, respectively, while figure 1(a') and (b') exhibit their magnified surface images. It is found that the C₆₀ growth occurs only on the GaAs surface (i.e. SiO₂ open area) at 200 °C. The facets appearing on the C₆₀ crystal surface suggest that the [111] oriented C₆₀ layers are grown on both GaAs (001) and (111)B substrates. The indices of facets formed on the C₆₀ surface are confirmed to be {100} and {110}. These images show that the surface morphology of C₆₀ crystals grown on GaAs (111)B is smoother than that grown on GaAs (001). Thus, the crystalline quality of C₆₀ films on GaAs (111)B seems to be better than those grown on GaAs (001). These hexagonal C₆₀ crystals are found to be thicker than the C₆₀ layer grown on unmasked substrate by 20 nm, and the side length of hexagonal C₆₀ crystals is longer than that of SiO₂ open area. These results suggest that C₆₀ molecules landing on SiO₂ mask migrate to the open area, and enhance the growth rate. The C₆₀ lateral growth is found to be less sensitive to the crystalline directions, i.e., in both <211> and <110> directions, the lateral growth is approximately 80 nm.

Figure 2 shows similar SEM images. In this case, however, the thickness is increased to 450 nm. Figures 2(a') and (b') exhibit their magnified surface images. Again, the surface morphology of C₆₀ crystal on GaAs (111)B is better than that grown on GaAs (001). In addition, the surface smoothness is improved significantly by increasing the thickness.

Figure 3 exhibits a topographic map of C₆₀ crystal on GaAs (111)B substrate

measured by AFM. The cross section image along the white line suggests that a part of C_{60} molecules landing on SiO_2 mask migrates to the open area, and enhances the C_{60} growth there. Since the volume of the C_{60} crystal grown by the vertical flux is easily estimated by the growth rate of unmasked (planer) substrate, the contribution of C_{60} molecules diffused from SiO_2 mask can be estimated by comparing the growth rates. The mean diffusion length of C_{60} molecules on SiO_2 mask at 200 °C thus is determined as 200-300 nm. It is also confirmed that the estimated diffusion length does not depend on the size of the opening area.

To investigate the crystalline quality of C_{60} films, XRD measurements are performed. XRD $2\theta/\omega$ scan shows that only (111) diffraction is observed from the C_{60} films on both substrates, indicating that the films are [111] oriented crystals with a fcc structure [7]. Figure 4 shows XRD ϕ (phi) scan patterns with $2\theta = 10.818^\circ$ [C_{60} (111) diffraction peak] and ψ (psi) = 70.5° of the C_{60} films on GaAs (001) (a) and (111)B substrates (b). In figure 4(a), the diffraction peaks have a six-fold symmetry, implying that the C_{60} films on GaAs (001) are twin crystals. The grooves seen on the C_{60} surface in figure 1(a) may be grain boundaries. In figure 4(b), the diffraction peaks have a three-fold symmetry, indicating that the C_{60} films grown on GaAs (111)B are [111] oriented single crystals. The crystalline quality of C_{60} films on GaAs (111)B substrates is better than that grown on GaAs (001) substrates. These results coincide with those of the surface roughness in figures 1 and 2.

Figure 5 shows SEM images of the C_{60} nanocrystals grown at 200 °C on GaAs

(001) (a), and GaAs (111)B substrates (b). The diameter of dot open area is about 100 nm. The size of the grown crystals is larger than that of SiO₂ open area, indicating that lateral growth of C₆₀ occurs. These images show that the C₆₀ epitaxial orientations are different between GaAs (001) and (111)B substrates. In figure 5(a), C₆₀ crystals have a four-fold symmetry, indicating that the epitaxial orientation of these C₆₀ crystals is [001]. On the other hand, the C₆₀ crystals in figure 5(b) have three-fold symmetry, indicating that the epitaxial orientation is [111].

Figure 6 shows the SEM images of C₆₀ crystals on narrow radial line open area. Figures 6(a) and 6(b) show the C₆₀ crystals on GaAs (001). Figures 6(c) and 6(d) show those grown on GaAs (111)B. The width of line open area is about 150nm. The {100} and {110} facets of C₆₀ crystals easily appear. These images suggest that C₆₀ crystals grown on GaAs (001) have a four-fold symmetry, and those grown on GaAs (111)B have a three-fold symmetry. It is interesting to note that the different epitaxial relationships are observed between the nanostructure growth and planer (wide area) growth on GaAs (001) substrate. Indeed, when the open area size is larger than 250nm, the growth crystals show [111] orientation, while, when it is below this value, the grown crystals show [001] orientation. Although it is reported that the different epitaxial orientation of C₆₀ crystals occurs on the different surface reconstructions of GaAs (001) substrate [9, 10], the present finding suggests that the crystal size is also one of the determining factors for the C₆₀ epitaxial orientation.

4. Conclusions

Fabrications of nanoscale structures of C_{60} crystals on GaAs substrates are successfully achieved with selective area epitaxy by MBE. The $\{100\}$ and $\{110\}$ facets appear on the C_{60} crystals, and the facets suggest that the $[111]$ oriented C_{60} layers are grown on both GaAs (001) and (111)B. The surface morphology of C_{60} crystals on GaAs (111)B is smoother than that grown on GaAs (001), indicating that the crystalline quality of C_{60} films on GaAs (111)B is better than that grown on GaAs (001). The surface roughness of C_{60} crystals becomes smaller as the thickness of C_{60} crystals increases. The mean diffusion length of C_{60} molecules on SiO_2 mask at 200 °C is estimated to be 200-300 nm from the volume of the C_{60} crystal grown by the lateral flux. It is confirmed that the estimated diffusion length does not depend on the size of the opening area. XRD ϕ (phi) scan patterns show that the C_{60} films on GaAs (001) are twin crystals, and the C_{60} films on GaAs (111)B are $[111]$ oriented single crystals. The C_{60} epitaxial orientations on narrow open area are different between GaAs (001) and (111)B substrates. The C_{60} crystals grown on GaAs (001) with narrow open area have a four-fold symmetry, indicating that the epitaxial orientation is $[001]$. The C_{60} crystals grown on GaAs (111)B with narrow open area have three-fold symmetry, indicating that the orientation is $[111]$.

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Figure Captions

Figure 1. SEM images of the hexagonal C_{60} crystals grown at 200°C. The thickness on the unmasked substrate is 180nm. The side length of SiO_2 open area is 3 μ m. Figure (a) and (b) show the C_{60} crystal on GaAs (001) and GaAs (111)B substrate, respectively. Figure (a') and (b') exhibit their magnified surface images.

Figure 2. SEM images of the hexagonal C_{60} crystals grown at 200°C. The thickness on the unmasked substrate is 450nm. Figure (a) and (b) show the C_{60} crystal on GaAs (001) and GaAs (111)B substrate, respectively.

Figure 3. Topographic map of the C_{60} crystal on GaAs (111)B substrate measured by AFM, and the cross section image along the white line.

Figure 4. X-ray diffraction ϕ (phi) scan patterns with $2\theta = 10.818^\circ$ [C_{60} (111) diffraction peak] and ψ (psi) = 70.5° of C_{60} films on GaAs (001) (a) and (111)B substrates (b).

Figure 5. SEM images of the nanoscale C_{60} crystals grown at 200°C on GaAs (001) (a), and GaAs (111)B substrates (b).

Figure 6. SEM images of the C_{60} crystals on narrow radial line open area. Figure (a) and (b) show the C_{60} crystals on GaAs (001). Figure (c) and (d) show those on GaAs (111)B.

JVST #30227 Figure 1

JVST #30227 Figure 2

JVST #30227 Figure 3

JVST #30227 Figure 4

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